

In other embodiments, there are at least 20 compounds, complexes or compositions on or in the substrate each having a different chemical formula. In still other embodiments, there are at least 40 or 90 or 124 compounds, complexes or compositions on or in the substrate each having a different chemical formula.

5 Because of the manner of forming combinatorial arrays, it may be that each compound, complex or composition may not be worked-up, purified or isolated, and for example, may contain reaction by-products or impurities or unreacted starting materials.

[0084] The catalytic performance of the compounds, complexes or compositions of
10 this invention can be tested in a combinatorial or high throughput fashion.

Polymerizations can also be performed in a combinatorial fashion, see, e.g., provisional U.S. Patent Application Nos. 09/211,982, filed December 14, 1998 and 09/239,223, filed January 29, 1999, each of which is herein incorporated by reference.

15 EXAMPLES

[0085] **General:** All reactions were performed under a purified argon or nitrogen atmosphere in a Vacuum Atmospheres glove box. All solvents used were of the anhydrous, de-oxygenated and purified according to known techniques.

Polymerizations were carried out in a parallel pressure reactor, which is fully
20 described in pending U.S. Patent Applications Nos. 09/177,170, filed October 22, 1998, 09/211,982, filed December 14, 1998 and 09/239,223, filed January 29, 1999, and WO 00/09255, each of which is incorporated herein by reference.

[0086] High temperature Size Exclusion Chromatography was performed using an automated "Rapid GPC" system as described in U.S. Patent 6,175,409, incorporated
25 herein by reference and U.S. Patent Application Nos. 09/285,363; 09/ 285,333; 09/285,335; or 09/285,392; each of which was filed on April 2, 1999 and each of which is incorporated herein by reference. In the current apparatus, a series of two 30 cm x 7.5 mm linear columns, with one column containing PLgel 10um, MixB and the other column containing PLgel 5um, MixC. The columns were calibrated using
30 narrow polystyrene standards. A flow rate of 1.5 mL/min. was used, with an injection volume of 40 µL of a polymer solution with a concentration of about 1 mg/mL, an oven temperature of 160°C, and the polymer samples dissolved in o-dichlorobenzene.

The concentration of the polymer in the eluent was monitored using an evaporative light scattering detector. All of the molecular weight results obtained are relative to linear polystyrene standards.

[0087] FTIR was performed on a Bruker Equinox 55 + IR Scope II in reflection mode with 16 scans, to determine the ratio of octene to ethylene incorporated in the polymer product, represented as the weight % (wt.%) of octene incorporated in the polymer (wt.% octene). Wt.% octene was obtained from ratio of peak heights at 1378 cm^{-1} and 4335 cm^{-1} . This method was calibrated using a set of ethylene/1-octene copolymers with a range of known wt.% octene content.

[0088] $\text{Er}(\text{OC}_6\text{H}_3\text{-2,6-}t\text{-Bu}_2)_3$ was prepared from the reaction of ErCl_3 (purchased from Alfa Aesar, ultradry anhydrous, 99.9%,) with 3 equivalents of $\text{LiOC}_6\text{H}_3\text{-2,6-}t\text{-Bu}_2$ in THF following the procedure employed by Lappert for the synthesis of $\text{Sm}(\text{OC}_6\text{H}_3\text{-2,6-}t\text{-Bu}_2)_3$ and other $\text{Ln}(\text{OAr})_3$ complexes (Lappert et al., *Inorganic Syntheses*, vol. 27 (1990), pp. 164-168, and Lappert et al., *J. Chem. Soc. Chem. Commun.*, 1983, pp. 1499-1501, each of which is incorporated herein by reference). $\text{Er}(\text{CH}(\text{SiMe}_3)_2)_3$ was prepared via the reaction of $\text{Er}(\text{OC}_6\text{H}_3\text{-2,6-}t\text{-Bu}_2)_3$ with 3 equivalents of $\text{LiCH}(\text{SiMe}_3)_2$ in hexane, using the procedure described by Lappert for the synthesis of $\text{La}(\text{CH}(\text{SiMe}_3)_2)_3$ and $\text{Sm}(\text{CH}(\text{SiMe}_3)_2)_3$ (Lappert et al., *J. Chem. Soc. Chem. Commun.*, 1988, pp. 1007-1009, incorporated herein by reference) and by Schaverien for the synthesis of $\text{Lu}(\text{CH}(\text{SiMe}_3)_2)_3$ and $\text{Y}(\text{CH}(\text{SiMe}_3)_2)_3$ (Schaverien et al., *Inorg. Chem.*, 1991, 30, pp. 4968-4978, incorporated herein by reference).

Examples 1 and 2: Ethylene-1-Octene Copolymerizations:

[0089] **Stock solutions:** Four stock solutions were prepared as follows: The “metal precursor solution” is a 30 mM solution of $\text{Er}(\text{CH}(\text{SiMe}_3)_2)_3$ in toluene (82 mg in 4 mL). The “ligand solution” is a 30 mM solution of 2,3-dihydrido-2,2-dimethyl-7-benzofuranol in toluene (200 mg in 40 mL toluene). The “group 13 reagent solution” is a 0.15 M solution of TEAL (triethylaluminum, AlEt_3) in toluene (0.41 mL of neat AlEt_3 plus 19.6 mL toluene). The “activator solution” is a 10 mM solution of triphenylcarbenium tetrakis(pentafluorophenyl)borate in toluene (74 mg in 8 mL toluene).

[0090] Preparation of the polymerization reactor prior to injection of catalyst

composition: A pre-weighed glass vial insert (the reactor vessel) and disposable stirring paddle were fitted to each reaction chamber of the parallel reactor. The reactor was then closed, and 4.85 mL of toluene followed by 0.15 mL of 1-octene was injected into each reaction vessel through a valve. The temperature was then set to 35 °C, and the stirring speed was set to 200 rpm, and the toluene/1-octene mixture was exposed to ethylene gas at 100 psi pressure. An ethylene pressure of 100 psi and a temperature of 35 °C were maintained, using computer control, until the end of the polymerization experiment.

[0091] Premix of metal precursor solution and ligand solution in 1 mL glass vial:

0.10 mL of the ligand solution was added to a 1 mL glass vial at room temperature. To this same vial was added, with mixing, 0.10 mL of the metal precursor solution, to form the metal-ligand combination solution.

[0092] Injection of solutions into the reactor vessel: After the toluene/1-octene mixture was saturated with ethylene at 100 psi pressure in the reaction vessel, and approximately 30 minutes after combining the metal precursor and ligand solutions in the 1 mL glass vial, 0.033 mL of the group 13 reagent solution followed immediately by 0.467 mL of toluene, were injected into the reaction vessel. About 30 seconds later, 0.067 mL of the metal-ligand combination solution followed immediately by 0.633 mL of toluene, were injected into the reaction vessel. About another 30 seconds later, an additional 0.100 mL of the "activator solution" followed immediately by 0.600 mL of toluene, were injected into the reaction vessel.

[0093] Polymerization: The polymerization reaction was allowed to continue for 1 hour, during which time the temperature and pressure were maintained at their pre-set levels by computer control. After 1 hour, the ethylene flow to the reactor vessel was stopped, and the ethylene pressure in the reactor vessel was vented.

[0094] Product work up: The glass vial insert, containing the polymer product and solvent, was then removed from the reactor and removed from the inert atmosphere dry box, and the volatile components were allowed to evaporate at room temperature in the air. After most of the volatile components had evaporated, the vial contents were dried thoroughly by evaporation at elevated temperature under reduced pressure. The vial was then weighed to determine the yield of polymer product. The polymer

product was analyzed by rapid GPC, as described above, to determine the molecular weight of the polymer produced, and by FTIR spectroscopy to determine the ratio of octene to ethylene incorporated in the polymer product, represented as the weight % of octene incorporated in the polymer. Results are presented in the Table 1:

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[0095] Table 1: Use of Erbium compounds as catalysts for ethylene/1-octene copolymerization:

Example #	$\mu\text{mol Er}$	Temp. ($^{\circ}\text{C}$)	Copolymer yield (g)	Mw	wt. % 1-octene
1	1.0	35	0.312	2.2×10^5	9
2	1.0	35	0.466	2.3×10^5	8

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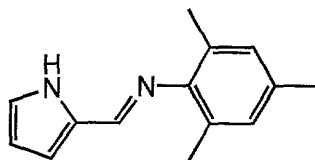
Examples 3-7: Ethylene-1-Octene Copolymerizations

[0096] In these examples a different protocol was followed as compared to Examples 1 and 2.

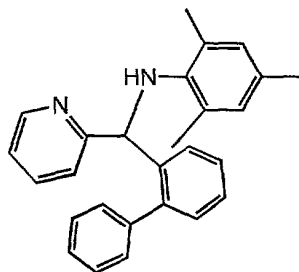
[0097] Ligands: The ligands chosen for these examples are as follows (see Table 2, below, showing which ligands are for which examples):

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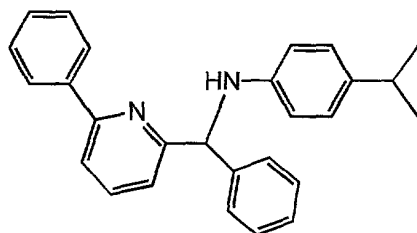
Ligand 1:



Ligand 2:



Ligand 3:



[0098] **Stock solutions:** The “group 13 reagent solution” is a 0.20 M solution of di-isobutylaluminum hydride (DIBAL-H). The “activator solution” is a 5 mM solution of N,N'-dimethylanilinium tetrakis(pentafluorophenyl)borate in toluene, heated to approximately 85 °C to fully dissolve the N,N'-dimethylanilinium tetrakis(pentafluorophenyl)borate.

[0099] **In situ preparation of erbium-ligand compositions:** Stock solutions were prepared as follows: The “metal precursor solution” is a 10 mM solution of $\text{Er}(\text{CH}(\text{SiMe}_3)_2)_3$ in toluene. The “ligand solutions” are 25 mM solutions of the ligands in toluene, prepared in an array of 1 mL glass vials by adding 0.040 mL of toluene to 1.0 μmol of the ligand in a 1 mL glass vial. To each 1 mL glass vial containing ligand/toluene solution was added 0.10 mL of the metal precursor solution (1.0 μmol), to form the metal-ligand combination solution. The resultant solutions are allowed to sit at room temperature for 1 hour prior to addition of the 1-octene, DIBAL-H, and N,N'-dimethylanilinium tetrakis(pentafluorophenyl)borate solutions, and injection into the reactor, as described below.

[0100] **Preparation of the polymerization reactor prior to injection of catalyst composition;** A pre-weighed glass vial insert (the reactor vessel) and a disposable stirring paddle were fitted to each reaction chamber of the parallel reactor. The reactor was then closed, 0.10 mL of a 0.02 M solution of DIBAL-H in toluene, then 3.8 mL of toluene, were injected into each pressure reaction vessel through a valve. The temperature was then set to the appropriate setting, and the stirring speed was set to 800 rpm, and the toluene / DIBAL-H mixture was exposed to ethylene gas at 100 psi pressure. An ethylene pressure of 100 psi and the temperature setting were maintained, using computer control, until the end of the polymerization experiment.

[0101] **Injection of solutions into the pressure reactor vessel:** After metal-ligand combination in the 1mL vial had been allowed to sit at room temperature for 1 hour, 0.030 mL of a 1.0 M 1-octene solution in toluene (30 μmol of 1-octene) was added to the 1mL vial. Next, 0.42 mL of 1-octene followed immediately by 0.38 mL of toluene, were injected into the pressurized, stirred, and heated, reaction vessel containing the toluene/DIBAL-H mixture saturated with ethylene at 100 psi pressure. Next, 0.030 mL (6 μmol) of the group 13 reagent (DIBAL-H) solution was added to

the 1 mL vial. About 90 seconds later, 0.240 mL (1.2 μ mol) of the "activator solution" was added to the 1mL vial. About another 30 seconds later, 0.220 mL of the 1 mL vial contents, followed immediately by 0.180 mL of toluene, were injected into the reaction vessel, followed immediately by a further 0.400 mL of toluene.

5 **[0102] Polymerization:** The polymerization reaction was allowed to continue for 15 minutes, during which time the temperature and pressure were maintained at their pre-set levels by computer control. After 15 minutes, the reaction was quenched by addition of an overpressure of carbon dioxide.

10 **[0103] Product work up:** The glass vial insert, containing the polymer product and solvent, was then removed from the reactor and removed from the inert atmosphere dry box, and the volatile components were removed in a centrifuge evaporator under reduced pressure. The vial contents were then dried thoroughly by evaporation at elevated temperature under reduced pressure. The vial was then weighed to determine the yield of polymer product. The polymer product was then analyzed by
15 rapid GPC, as described above, to determine the molecular weight of the polymer produced, and by FTIR spectroscopy to determine the ratio of octene to ethylene incorporated in the polymer product, represented as the weight % of octene incorporated in the polymer. Results are presented in the Table 2:

20 **[0104]** Table 2: Use of Erbium compounds as catalysts for ethylene/1-octene copolymerization:

Example # and Ligand #	μ mol Er	Temp. ($^{\circ}$ C)	Copolymer yield (mg)	Mw	wt. % 1-octene
Ex. 3, L1	0.5	110	55	2.7×10^5	5
Ex. 4, L2	0.5	110	36	8.8×10^4	4
Ex. 5, L3	0.5	110	36	1.3×10^5	5
Ex. 6, No Ligand	0.5	110	20	1.1×10^5	7
Ex. 7, No Ligand	0.5	75	172	7.5×10^4	4

25 **[0105]** It is to be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should, therefore, be

determined not with reference to the above description, but should instead be
determined with reference to the appended claims, along with the full scope of
equivalents to which such claims are entitled. The disclosures of all articles and
references, including patent applications and publications, are incorporated herein by
5 reference for all purposes.